

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 September 2003 (18.09.2003)

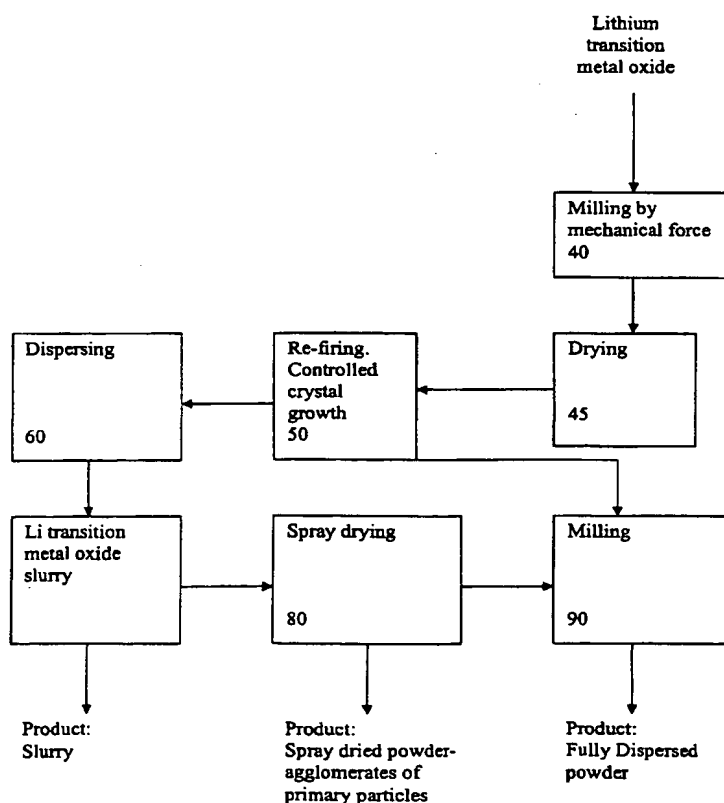
PCT

(10) International Publication Number
WO 03/076338 A1

- (51) International Patent Classification⁷: **C01G 45/00**, (74) Agent: **NICHOLS, Peter, G.**; Brinks Hofer Gilson & Li-one, P.O. Box 10087, Chicago, IL 60610 (US).
- (21) International Application Number: **PCT/US03/06989**
- (22) International Filing Date: **7 March 2003 (07.03.2003)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
60/362,723 **8 March 2002 (08.03.2002)** **US**
- (71) Applicant: **ALTAIR NANOMATERIALS INC.**
[US/US]; 204 Edison Way, Reno, NV 89502 (US).
- (72) Inventors: **SPITLER, Timothy, M.**; 102 Rachel Street, Fernley, NV 89408 (US). **PROCHAZKA, Jan**; 91 Bell Street, Apt. 4, Reno, NV 89503 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: **PROCESS FOR MAKING NONO-SIZED AND SUB-MICRON-SIZED LITHIUM-TRANSITION METAL OXIDES**



(57) Abstract: A process is provided for making nano-sized or sub-micron sized oxides of lithium and a transition metal. The desired size is generally in the range 10 nm to 1000 nm and preferably in the range 10 nm to 100 nm. The particles have a narrow size distribution. The process includes milling and refiring under controlled conditions so that crystallites of the desired particle size are grown.

WO 03/076338 A1



Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

**PROCESS FOR MAKING NANO-SIZED AND
SUB-MICRON-SIZED LITHIUM-TRANSITION METAL OXIDES**

[0001] The present application claims priority to USSN 60/362,723
5 filed March 8, 2002, the entire contents of which is hereby incorporated by
reference.

[0002] The present invention relates to a process for producing
nano-sized and sub-micron-sized lithium titanate, lithium manganate, lithium
cobalt oxide and other oxides of lithium and transition metals. It covers parts
10 of the process and the product of the process. The starting material is a
coarse oxide with low surface area. The product made according to the
process of the present invention has a high surface area and a narrow particle
size distribution.

BACKGROUND OF THE INVENTION

15 **[0003]** Lithium-transition metal oxides are materials presently used
or under development for the electrodes of lithium ion batteries. The
transition metals Co, Mn, Ni, Ti, and V have received particular attention for
this application. Recently, it has become apparent that a smaller particle size
and a narrower particle size distribution are beneficial for producing
20 electrodes, which retain their charging capacity at high charging and
discharging rates.

[0004] A method to prepare lithium titanate from inorganic solutions
or suspensions is described in US Pat. Appln. Pub. 2003/0017104 A1, the
relevant portions of which are incorporated herein by reference. That
25 application describes a process to produce lithium titanate crystallites. The
process achieves good phase and size control in the range of 5 to 2000 nm.
In general, the process includes providing a source of lithium titanate with a
particle size smaller than the desired particle size and re-firing the lithium
titanate under conditions to produce a final lithium titanate having a desired
30 particle size with a narrow size distribution and controlled surface area.

[0005] That application describes that a source of lithium titanate is
from a process that includes forming a blend that comprises titanium and
lithium. The blend is evaporated to form homogeneous particles containing a
lithium salt and titanium dioxide. The evaporation is conducted at a
35 temperature above the boiling point of the solution in the blend but below the

temperature where reaction of the lithium salt and the titanium dioxide occurs. The homogeneous particles are calcined to form lithium titanate.

[0006] The lithium titanate is milled or crushed to a size smaller than the desired size of the final product. Finally, the milled lithium titanate is re-fired under conditions to produce lithium titanate having a desired surface area and size distribution.

[0007] The blend of titanium and lithium can be provided from a variety of suitable sources. For example, the blend of titanium and lithium is provided as aqueous chloride solutions of titanium and lithium. Alternatively, the blend of titanium and lithium is provided as a suspension of amorphous titanium dioxide in a lithium solution. In this instance, the lithium solution can be formed from a source of lithium selected from the group consisting of lithium chloride, lithium nitrate, lithium hydroxide, lithium sulfate, lithium oxide, lithium fluoride, lithium bromide, and mixtures thereof. In yet another alternative, lithium titanate, made by any known means and having a particle size smaller than the particle size of the desired product, can be used as the source of lithium and titanium for the re-firing step, where crystals are grown to the desired size.

[0008] A method to prepare mixed metal oxides and metal oxide compounds is also described in US Pat. Appln. Publication US 2002/0071806 A1 the relevant portions of which are incorporated herein by reference. This method applies to mixed oxides of lithium and transition metals. Products made according to this Patent Application can be used as starting materials for the process of the present invention.

[0009] Materials commercially available for the manufacture of battery electrodes generally have a wide particle size distribution and include large particles of several microns in size as well as very fine dust. Therefore, there is a need for materials having a narrow size distribution and having a controlled surface area for such applications as electrodes for batteries.

SUMMARY OF THE INVENTION

[0010] The present invention provides a process to produce lithium-transition metal oxides in the range 10 to 1000 nm, and preferably 10 to 100 nm with a narrow particle size distribution. The phrase narrow particle size

distribution means that the particle size of the lithium-transition metal oxide is within 10 nm to 1,000 nm with a standard deviation of no more than 20%.

[0011] In general, the process starts from a coarse oxide of lithium and a transition metal. The coarse oxide of lithium and a transition metal can be provided by any suitable method including using commercially available coarse oxides. The process produces nano-sized crystals through a combination of milling, dispersion and calcining (re-firing) steps. The transition metal may be any metal commonly defined as transition metal, including but not limited to Ti, Co, Mn, V, Fe, and Ni.

10 BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 is a flow sheet of the general aspect of the process.

[0013] Fig. 2 is a flow sheet of the process according to one embodiment of the present invention, where the starting material is lithium titanate spinel and the final product is a slurry containing nano-sized particles.

15 [0014] Fig. 3 is a flow sheet of the process according to the invention, where the starting material is lithium manganate LiMn_2O_4 or lithium cobalt oxide LiCoO_2 and the final product is a nano-sized dispersed lithium manganate or lithium cobalt oxide powder.

[0015] Fig. 4 is a scanning electron micrograph of lithium titanate spinel of about 1 to 2 μm in size, serving as starting material for the process of the present invention.

[0016] Fig. 5 is a scanning electron micrograph showing lithium titanate spinel products of different particles sizes, produced following the process of the present invention.

25 [0017] Fig. 6 is a scanning electron micrograph showing commercial lithium manganate used as starting material for the process of the present invention.

[0018] Fig. 7 is a scanning electron micrograph showing lithium manganate products of different particle sizes produced following the process of the present invention.

30 DESCRIPTION OF THE INVENTION

[0019] According to the present invention, a process for making lithium-transition-metal oxides is provided. In this process, a lithium transition-

metal oxide is milled or crushed to a size smaller than the desired size of the final product. The milled or crushed lithium-metal oxide is re-fired under controlled conditions to produce lithium-transition-metal oxide (e.g., lithium titanate) having a desired surface area and size distribution. Further
5 processing may include dispersion, remilling, slurring and spray drying and the final product may be a slurry, a spray dried powder consisting of agglomerates of nano-particles, or a fully dispersed powder.

[0020] Turning now to Figure 1, a flow sheet according to the general process is shown. Coarse lithium-transition-metal oxide particles are
10 milled 40 to a desired median size. After milling, the lithium-transition-metal oxide (e.g., lithium titanate) is dried 45 and re-fired in a controlled temperature furnace 50 to produce particles having a desired size and size distribution.

[0021] Thereafter, the particles produced from the re-firing can be dispersed 60 or can be milled 90. If the particles are dispersed, they may be
15 further processed or may be left as is. Further processing may include forming a lithium-transition metal oxide slurry 70, which can be further processed by spray drying 80 to produce spray-dried powder agglomerates that consist of primary particles. The spray-dried powder agglomerates may be sold or may be further processed by milling 90 to produce a fully dispersed
20 powder.

[0022] The specific steps of the process will be explained in more detail below.

Starting Material

[0023] The starting material of coarse particles can be made by any
25 method. For example, commercially available coarse lithium-transition-metal oxide particles can be used as the starting material. Alternatively, as noted above, one suitable method is described in US Pat. Appln. Publication 2003/0017104 A1, the relevant portions of which are incorporated herein by reference. While the process described in US Pat. Appln. Publication
30 2003/0017104 is directed to lithium titanate; it has now been found that the described process can be used to make the lithium transition-metal oxides described in the present application. In addition, a related method is

described in US Pat. Appln. Publication 2002/0071806, the relevant portions of which are incorporated herein by reference.

[0024] According to those processes, a blend of a transition metal and lithium is provided by providing a source of lithium and a source of a transition metal. This blend may be referred to herein as the lithium-transition-metal blend or the transition-metal-lithium blend.

[0025] After the lithium-transition-metal blend is created, the blend is evaporated. The evaporation process is conducted above the boiling point of the liquid in the blend and below the temperature where significant reaction of the lithium and the transition-metal compounds occurs or where there is significant crystallization of lithium-transition-metal.

[0026] The evaporation is conducted under conditions to achieve substantially total evaporation and to form an intermediate. In particular, the evaporation is conducted at a temperature higher than the boiling point of the blend but lower than the temperature where significant crystal growth of an oxide phase occurs. The evaporation may be conducted at a temperature higher than the boiling point of the blend but lower than the calcination temperature of the intermediate.

[0027] The term "substantially total evaporation" or "substantially complete evaporation" refers to evaporation of greater than 85% of the free water content, preferably greater than 90% of the free water and more preferably greater than 95% of the free water present in the feed solution. The term "free water" is understood and means water that is not chemically bound and can be removed by heating at a temperature below 150° C. After substantially total evaporation or substantially complete evaporation, the intermediate product will have no visible moisture present.

[0028] The evaporation process is performed in a manner to control the physical form of the product. Preferably, the evaporation process is accomplished by spraying the blend while it is heated at a temperature in the range from about 120°C to about 350°C, and desirably in the range from about 200°C to about 250°C. This process may be conducted in a spray dryer.

[0029] As noted in US Pat. Appln. Pub. 2003/0017104 A1, the evaporation process may be conducted in such a manner as to form a film of a mixture of a lithium compound and an amorphous oxidized transition-metal compound. In this regard, the evaporation process may be conducted in such a way as to form a thin film of lithium salt on the preexisting particles of amorphous oxidized transition-metal compound.

[0030] In both cases, through control of the operating parameters, including temperature and concentration of transition-metal and lithium, the characteristics of the solid intermediate product can be reliably controlled within a fairly narrow range. For example, the product resulting from injection in a spray dryer, will generally be composed of hollow spheres or parts of spheres. The dimensions of the spheres may vary from less than 0.1 μm to 100 μm or more in diameter and a shell thickness in the range from about 30 nanometer to about 1000 nanometer or more. The structure of the shell consists of an intimate mixture of transition-metal and lithium compounds.

[0031] Evaporation by spraying also has the advantage of direct processing of the solution so that a homogeneous intermediate product is formed and so that evaporation of water and acid is simultaneously accomplished. Preferably, from about 90% to about 99% of any aqueous material is evaporated.

[0032] The product resulting from the evaporation step is calcined at a temperature and for a length of time sufficient to convert the mixture of transition-metal and lithium compounds to lithium transition metal oxide of the desired structure and particle size. Calcination temperatures can range between about 600°C to 950°C. Desirably, the calcination is conducted at temperatures ranging from about 700° C to about 900° C. The calcination time varies over a wide range, from about 1 hour to as long as 36 hours. Desirably, the calcination time is in the range from about 6 hours to about 12 hours. Lower temperatures will require longer calcination times. The product of calcination shows a structure of individual units that can be broken up by milling into particles of the desired median size and size distribution.

[0033] During calcination, the lithium salt reacts with oxygen and water in the furnace atmosphere to release, for example, HCl gas or nitrous

and nitric oxides or other gases formed by decomposition of the salt present in the original solution. These gases may be recovered. The calcination conditions are chosen such that contact with oxygen is sufficient to substantially convert the mixture to a lithium transition-metal oxide with low impurity level.

[0034] The product of calcination may contain traces of the original lithium salt used as feed. To remove the traces of salt, the particles may be subject to one or several wash cycles. In each cycle, the particles are mixed with water and are separated by settling or filtration. The washing step is particularly useful if the lithium salt used is lithium chloride.

Milling

[0035] The lithium-transition metal oxide is suspended in water and milled in a horizontal or vertical pressure media mill to crush the crystals to a size smaller than the size desired in the final product.

Drying

[0036] The wet-milled particles are dried by any known means. For example, wet-milled particles may be dried in a spray drier at a temperature from about 120° to about 350°C, desirably from about 200° to about 250°C. Drying may also be part of the re-firing process.

Re-firing

[0037] After milling or drying, the product is re-fired in a controlled-temperature furnace to make a product with a well-controlled specific surface area, consisting of regular-shaped crystals with a narrow size distribution. The refiring temperature is chosen to achieve the desired particle size and surface area of the product. In general, the re-firing temperature is between about 250° and 900° C, and the BET surface area of the re-fired product is in the range 5 to 100 m²/g, with the higher re-firing temperature corresponding to the lower specific surface area.

Dispersing

[0038] After the refiring step, the product may be dispersed to separate the agglomerates formed during re-firing into distinct nano-sized particles. This step is generally accomplished after slurring the product in

water. Alternatively, the product of the re-firing step may be milled 90, i.e., dry-milled, preferably in a jet-mill.

Further processing

5 **[0039]** Depending on the destination of the final product, the product from the dispersing step can be kept as a slurry, or spray-dried, or spray-dried and jet-milled as indicated in Fig. 1.

[0040] The following examples illustrate, but do not limit, the present invention.

EXAMPLES

10 **Example I**

[0041] Lithium titanate made by spray drying according to US Pat. Appln. Publication 2003/0017104 A1 and described above was further calcined in an oxidizing atmosphere at a temperature of 800° C for 12 hours. The product after calcination consisted of crystals of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of about 400 to
15 about 1000 nm in size. Figure 4 is a scanning electron micrograph of the product serving as starting material for the process of the present invention.

[0042] The product of the calcination step was further suspended in water and milled with 0.4 to 0.6 mm zirconia grinding media for 8 hours. The BET surface area of this product was 135 m²/g. This product was refired at
20 constant temperature for 3 hours. Fig. 5 shows electron micrographs of the product obtained after refiring at 900°, 650°, 500°, and 400° C respectively. The particle size was about 100 nm at 400° C, and increased to about 200, 500 and 1000 nm respectively at the higher temperatures. The micrographs
 . show well-formed crystals with a narrow size distribution.

Example II

[0043] Commercial lithium manganate, of particle size and shape shown in Fig. 6, was slurried as a 40 weight % suspension in water and was milled in a Premier Mill bead mill for 20 h. The product of this operation was
5 dried, and then calcined in ceramic trays placed in a constant temperature furnace for 3 hours. The results of calcinations at different temperatures are given in the Table below:

Calcination temperature (C)	Particle size (nm)
uncalcined	15
400°	20
450°	30
500°	50

10 **[0044]** Electron micrographs of each of the samples are shown in Fig. 7. All calcined crystals are well formed and show narrow size distributions.

What is claimed:

1. A process for producing a nano-sized or sub-micron oxide of lithium and a transition metal comprising:
 - a. milling a coarse lithium transition-metal oxide; and,
 - 5 b. re-firing the lithium transition-metal oxide
2. The process of claim 1 wherein the lithium transition-metal oxide is tetra lithium titanate spinel
- 10 3. The process of claim 1 wherein the lithium transition-metal oxide is LiCoO_2 .
4. The process of claim 1 wherein the lithium transition-metal oxide is LiMn_2O_4 .
- 15 5. The process of claim 1 wherein the milling is accomplished by wet-milling in a bead mill.
6. The process of claim 1 further comprising:
 - 20 a. dispersing the product resulting from re-firing to liberate crystallites; and,
 - b. slurring the crystallites to form a suspension.
7. The process of claim 1 further comprising milling the product resulting
25 from re-firing to form a dispersed powder.
8. The process of claim 6 further comprising spray-drying the suspension.
9. The process of claim 8 further comprising milling the spray-dried
30 product to form a dispersed powder.
10. A lithium-transition metal oxide with a particle size between 10 nm and 1000 nm and a standard deviation of no more than 20%.

11. A lithium-transition metal oxide with a particle size between 10 nm and 1000 nm and a standard deviation of no more than 20% made according to the process of any of claims 1-9.

FIG. 1

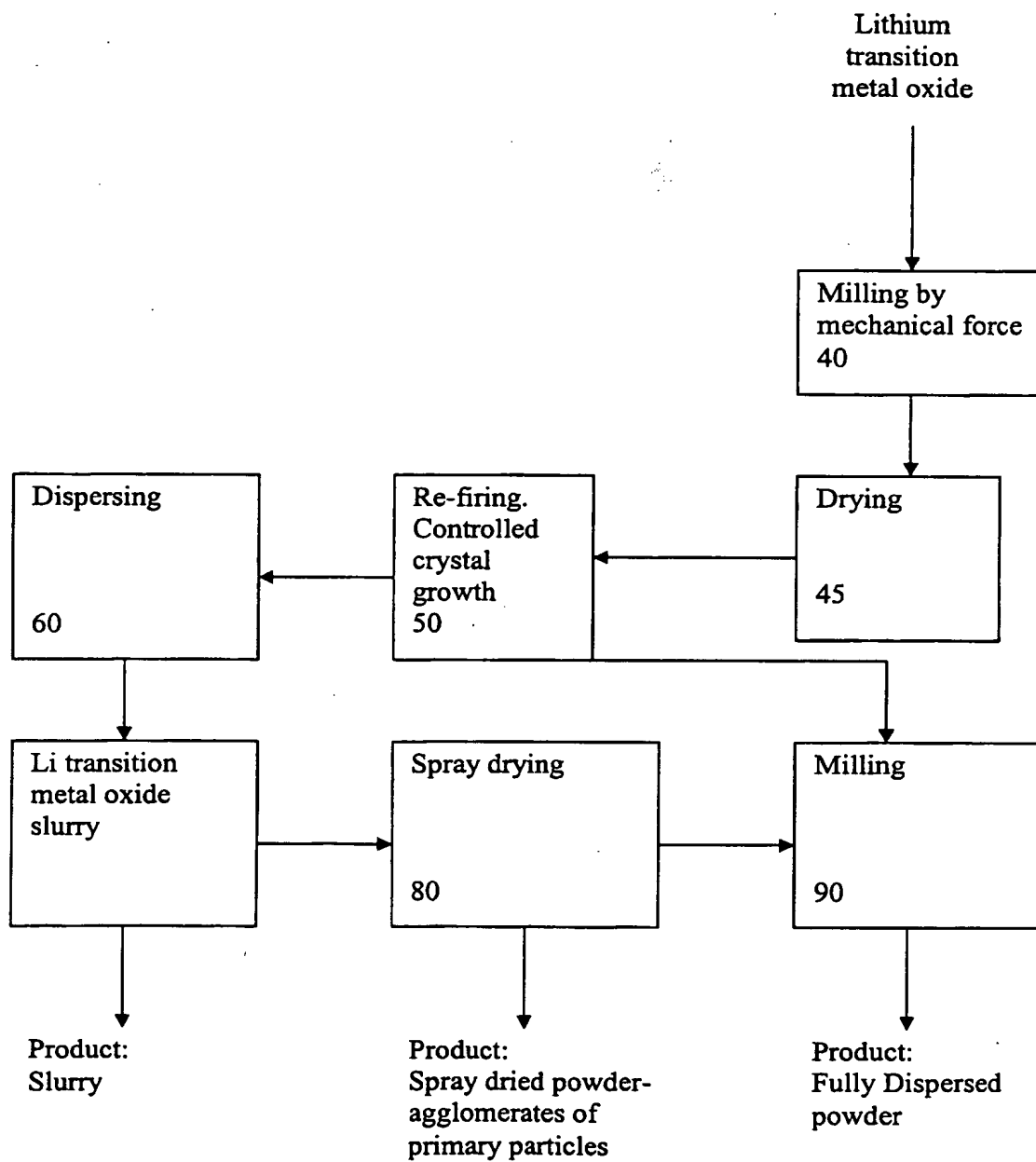


FIG. 2

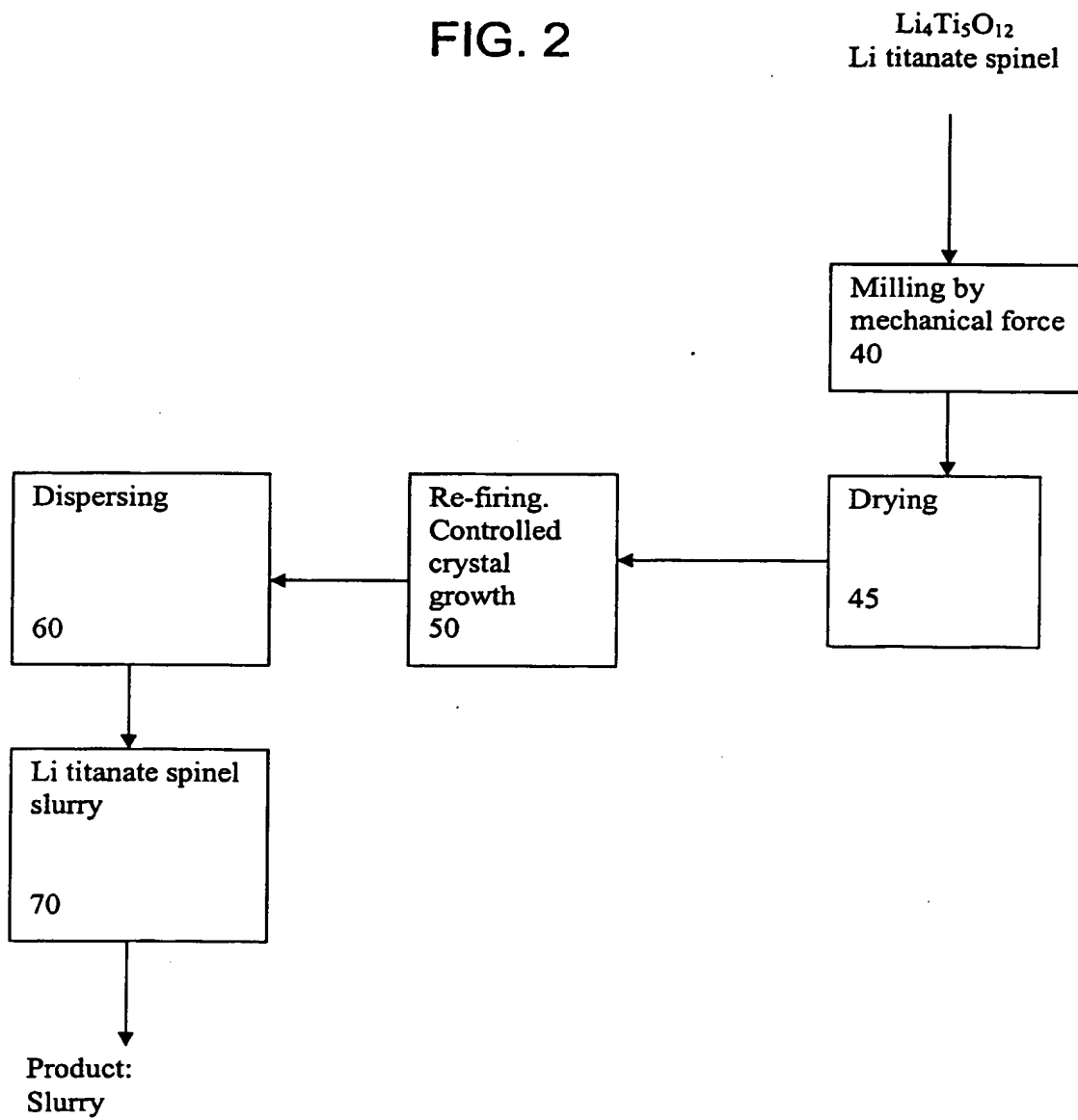


FIG. 3

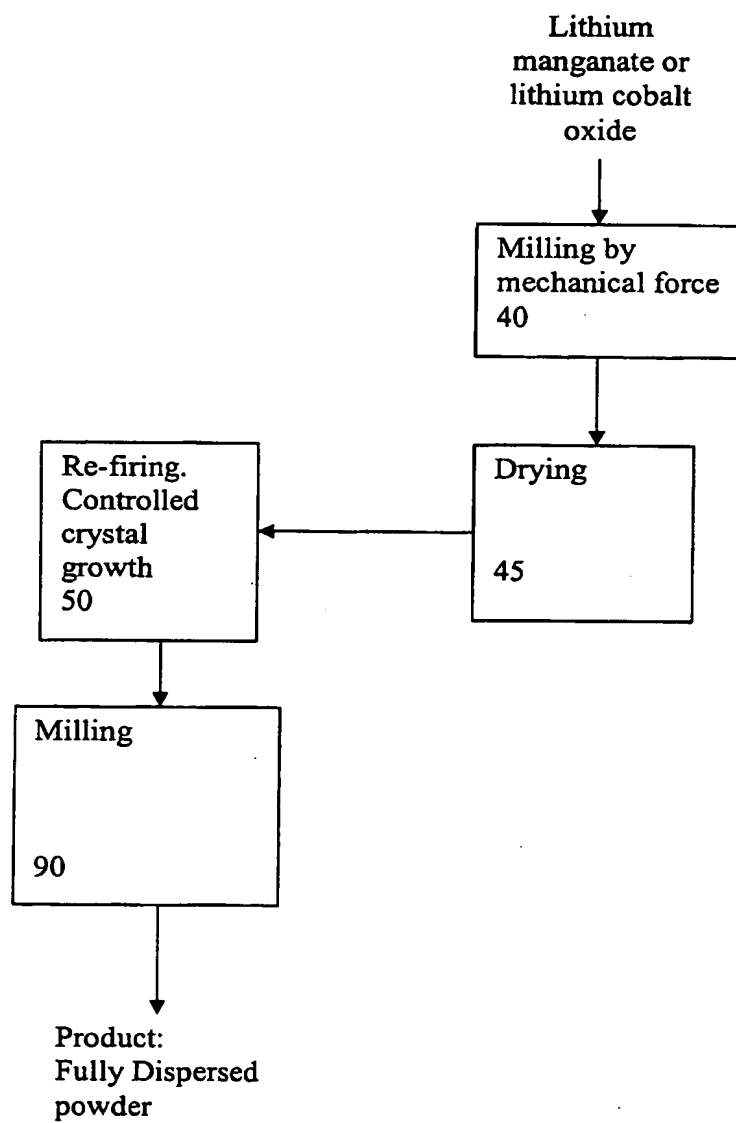


FIG. 4

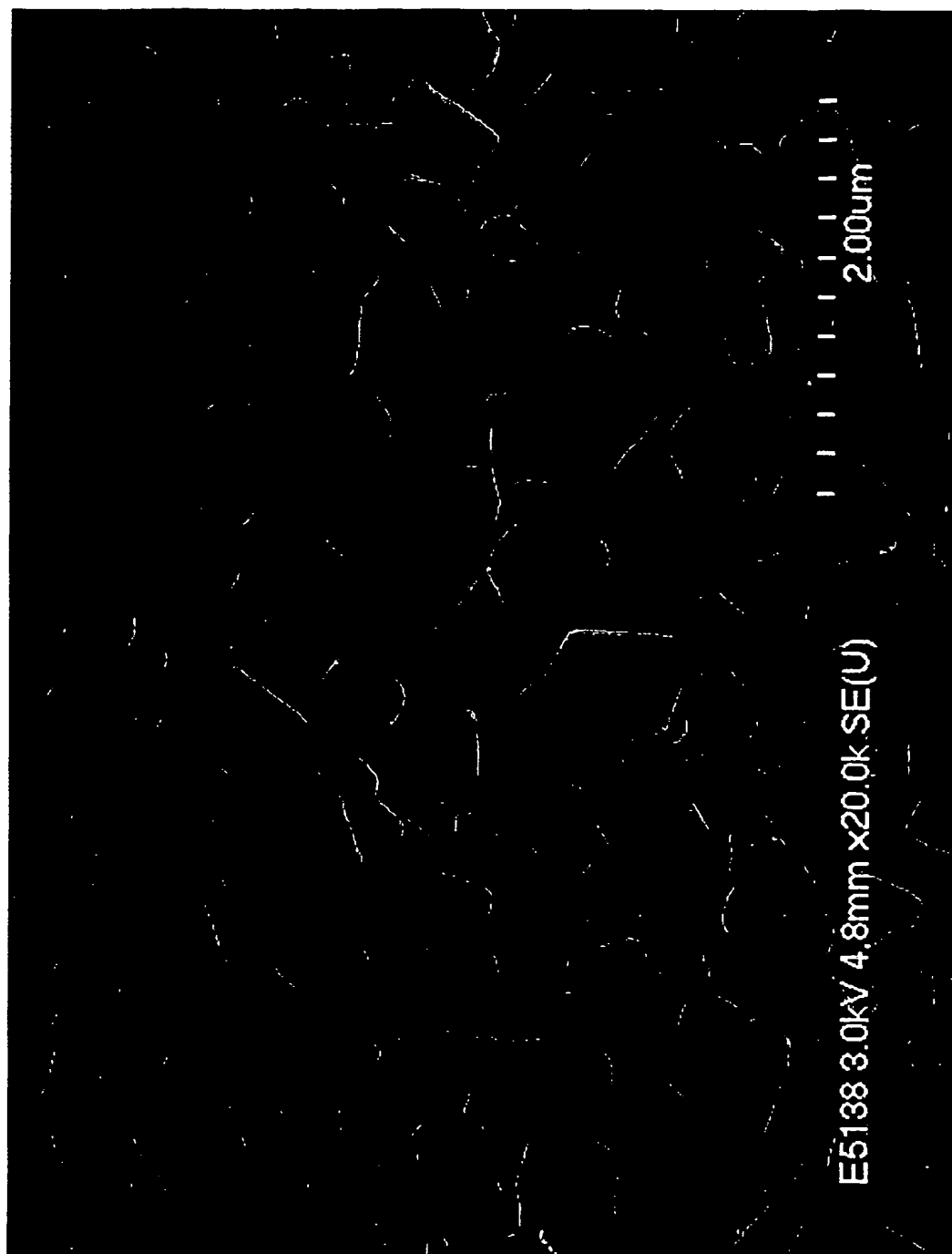


FIG. 5

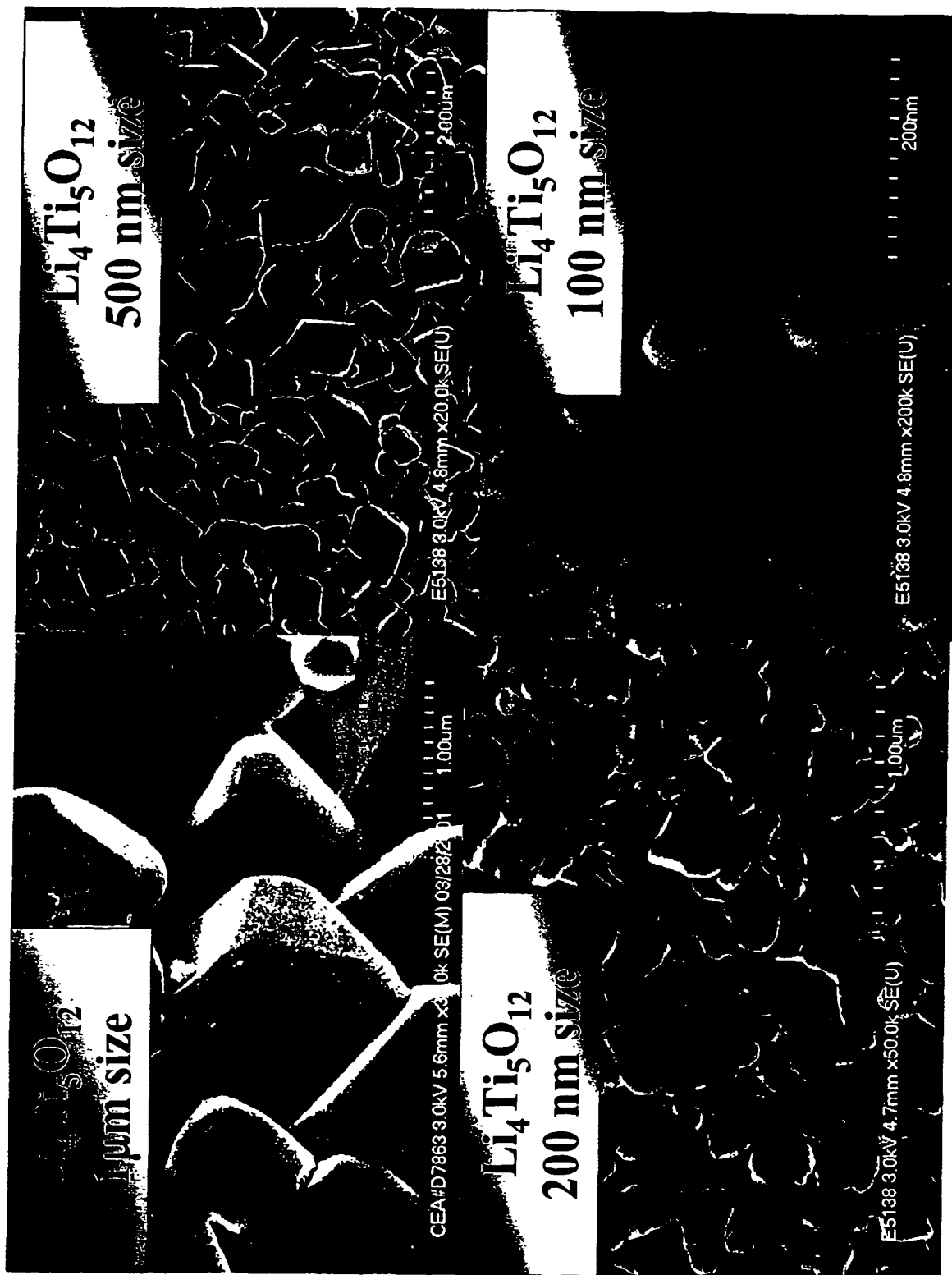


FIG. 6

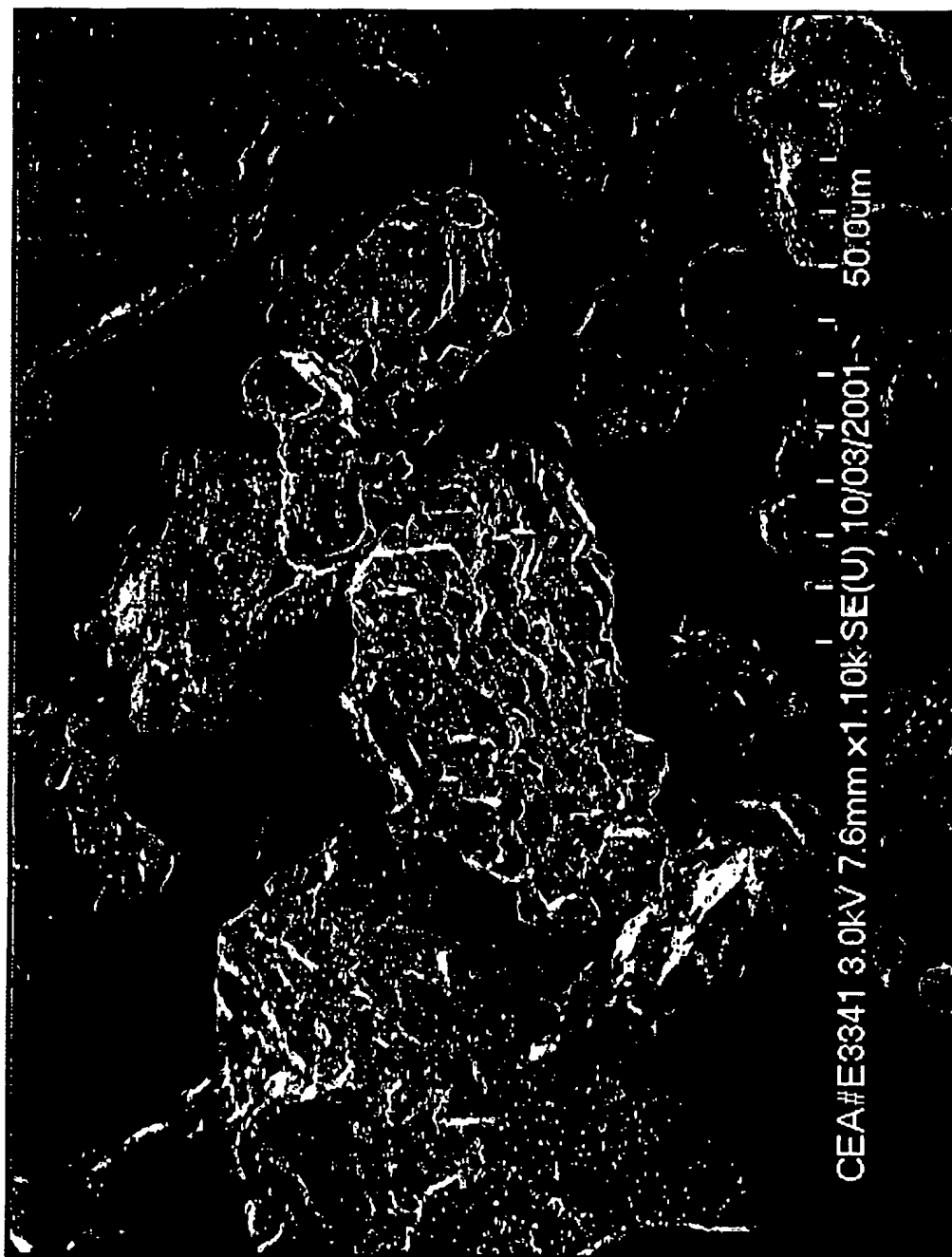
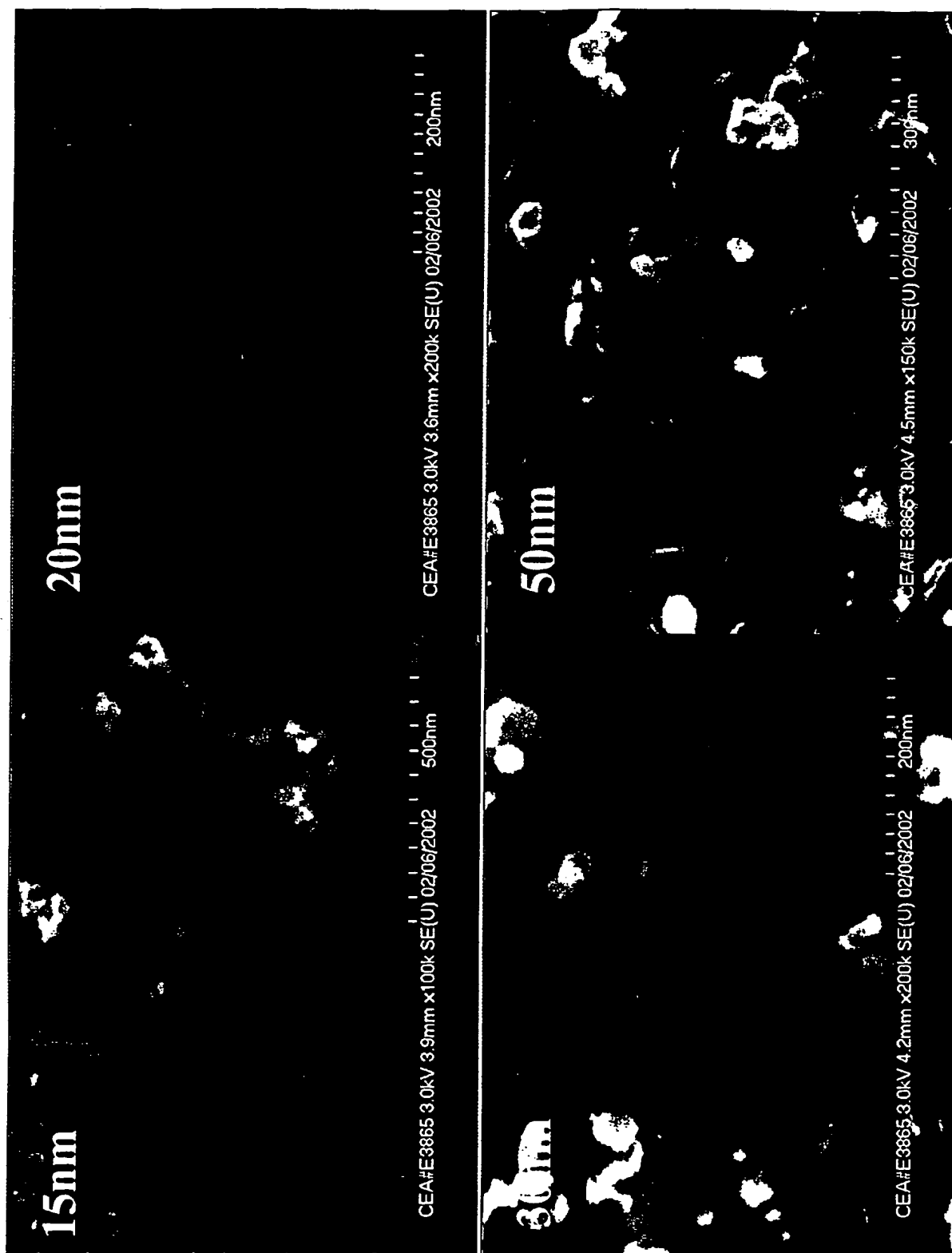


FIG. 7



INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/US 03/06989

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01G45/00 C01G51/00 C01G1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LUNDBLAD A ET AL: "Effect of sintering procedures in development of LiCoO ₂ -cathodes for the molten carbonate fuel cell" JOURNAL OF POWER SOURCES, ELSEVIER SEQUOIA S.A. LAUSANNE, CH, vol. 90, no. 2, 1 October 2000 (2000-10-01), pages 224-230, XP004213465 ISSN: 0378-7753 page 225	1,3,6,7
A	---	2,8-11
X	EP 1 026 765 A (NGK INSULATORS LTD) 9 August 2000 (2000-08-09) paragraph '0027!; figure 1	1,4
Y	---	2
A	---	3,5-11
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

7 July 2003

Date of mailing of the international search report

15/07/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Werner, H

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/06989

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PROSINI P P ET AL: "Li4Ti5O12 as anode in all-solid-state, plastic, lithium-ion batteries for low-power applications" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 144, no. 1-2, 1 September 2001 (2001-09-01), pages 185-192, XP004305622 ISSN: 0167-2738	2
A	page 186	1,3-11
X	US 2001/014421 A1 (SHIRAKAWA AKIHIKO ET AL) 16 August 2001 (2001-08-16) example 1	1,4
Y		2
A		3,5-11
Y	ROBERTSON A D ET AL: "New inorganic spinel oxides for use as negative electrode materials in future lithium-ion batteries" JOURNAL OF POWER SOURCES, ELSEVIER SEQUOIA S.A. LAUSANNE, CH, vol. 81-82, September 1999 (1999-09), pages 352-357, XP004363177 ISSN: 0378-7753	2
A	page 352 -page 353	1,3-11
X	DE 198 37 625 A (SAMSUNG DISPLAY DEVICES CO LTD) 4 March 1999 (1999-03-04) column 2, line 7-23 column 4, line 13-27	1,4
X	WO 98 41476 A (WAGHRAY AKSHAY ;EVEREADY BATTERY INC (US); KUMTA PRASHANT N (US);) 24 September 1998 (1998-09-24) page 21, line 13-30; figure 17	10,11
X	US 5 807 532 A (SATO KEIJI ET AL) 15 September 1998 (1998-09-15) figure 1; example 1	10,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/06989

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1026765	A	09-08-2000	JP	2000228195 A	15-08-2000
			EP	1026765 A1	09-08-2000
			US	2002122767 A1	05-09-2002
US 2001014421	A1	16-08-2001	JP	2001273900 A	05-10-2001
DE 19837625	A	04-03-1999	KR	261120 B1	01-07-2000
			DE	19837625 A1	04-03-1999
			GB	2328684 A , B	03-03-1999
			JP	11149926 A	02-06-1999
WO 9841476	A	24-09-1998	AU	6864098 A	12-10-1998
			CN	1258264 T	28-06-2000
			EP	0968135 A1	05-01-2000
			JP	2001526620 T	18-12-2001
			WO	9841476 A1	24-09-1998
US 5807532	A	15-09-1998	WO	9622943 A1	01-08-1996
			JP	2977909 B2	15-11-1999